ANALYTICAL APPLICATIONS OF MODIFIED PHENANTHROLINIUM AND RELATED IONS

BY

JOHN EDWARD DEVRIES

A.B., Hope College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS
1944

ANALYTICAL APPLICATIONS OF MODIFIED PHENANTHROLINIUM AND RELATED IONS

BY

JOHN EDWARD DEVRIES

A.B., Hope College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS
1944

ACKNOWLEDGMENT

The problems studied in connection with this thesis were suggested by, and carried out under the direction of, Professor G. Frederick Smith. Appreciation is expressed for this co-operation.

ANALYTICAL APPLICATIONS OF MODIFIED PHENANTHROLINIUM AND RELATED IONS

INTRODUCTION

During the past decade, a great deal of analytical importance has become attached to a group of compounds exhibiting the active functional group $=N-\overset{|}{C}-\overset{|}{C}-N=$. Particularly significant in this group are 2,2′-bipyridyl, 1,10-phenanthroline, and several substituted phenanthrolines all of which are best known in the form of their ferrous complexes. The use of some of these complexes as ideal oxidation-reduction indicators has been well established and extends to a host of reactions in this field. No less important is the application of the intensely colored complexes for the colorimetric determination of iron.

Investigations on bipyridyl have been limited by the difficulty in synthesizing this compound. A study was therefore undertaken to try to devise an improved synthesis of the material.

Outside of the parent compound, very little information has been reported on the derivatives of 1,10-phenanthroline. It was the purpose of this investigation to extend the colorimetric methods to several phenanthroline derivatives while applying the method to a study of their solubilities. Extension of the solubility studies was undertaken in applying the complexes in the quantitative precipitation of various anions.

II. SYNTHESIS OF 2,2′-BIPYRIDYL.

The first synthesis and extensive studies on 2,2′-bipyridyl were performed in 1888 by Blau,[1]. In view of the difficulty in substituting in the pyridine nucleus, a roundabout attack was employed in synthesizing the compound through the pyrolysis of copper picolinate. The complexing properties of the red compound were very thoroughly investigated by Blau himself[2] so that practically all the information at hand today was touched upon in some phase of his work.

More than thirty years passed before new attempts at synthesizing 2,2′-bipyridyl were made, and then practically all inves-

tigations were directed toward the general method of pyrolyzing pyridine catalytically. Most of this work is summarized in the report of Burstall[3] on polypyridine derivatives.

Inasmuch as most previous methods employed dehydrogenation or debromination of pyridine and bromopyridine to generate the pyridyl radical, a reaction was chosen which might produce this radical under such conditions that the dimerization would occur without employing the vigorous conditions necessary for direct dehydrogenation or debromination.

Mechanisms were proposed for two Grignard reactions both of which appeared promising as a means of producing pyridyl radical. Both of the reactions were investigated with the result that a feasible yield of bipyridyl was obtained when ethyl magnesium bromide was allowed to react with cobalt chloride in the presence of 2-brompyridine. The mechanism postulated involves the formation of an active sub-halide (CoCl·) which is regenerated to cobaltous ion by the oxidizing effect of brompyridine. Pyridyl radical is thus formed. A 20 percent of bipyridyl was obtained.

The other Grignard reaction, in which 2-pyridyl magnesium bromide was allowed to react with cobalt chloride in the presence of ethyl bromide, gave a 13 percent yield of the product, the yield being decreased probably on account of the insolubility of the pyridyl magnesium bromide.

A second synthesis of 2,2′bipyridyl was investigated based on the fact, previously reported by Willink and Wibaut[4], that upon determination of the melting point of 3,3′-dicarboxy-2,2′-bipyridyl, decomposition occurred with liberation of bipyridyl.

In the present study, 80 percent yields of the dicarboxylic acid was obtained from the alkaline permanganate oxidation of either 1,10-phenanthroline or its ferrous perchlorate complex. Decarboxylation of the acid was carried out successfully in two ways. By using biphenyl as a solvent for the reaction and by dry distilling the copper salt of the dicarboxylic acid. In each case a yield of 40 percent was obtained.

Of particular interest was the recovery of the dicarboxylic acid from the extremely stable ferrous perchlorate complex. Previous attempts by the author to recover the base, in any form, from the complex had been unsuccessful.

III. DETERMINATIONS OF SOLUBILITIES OF SUBSTITUTED 1,10-PHENANTHROLINE COMPLEXES.

No previous quantitative determinations of any solubilities of ferroin complexes has been reported. The insolubility of certain of the complexes was observed by Blau[2]. A semi-quantitative study of the solubilities of several of the complexes was carried out by Taylor[5]. In the present study a colorimetric method was applied in determining the solubilities of some of the complexes. Thus, by comparing the color of the saturated solutions of the complex with previously prepared standards, a quantitative estimation of the concentration of the complex was obtained. Absorption spectra, in the wave length range 400-700 millimicrons were measured at several different known concentrations of the complexes and the resulting calibration curves, relating extinction to concentration of complex, were plotted. Solubilities of the complexes were determined in various solvents. The procedure for the solubility determination consisted of essentially three steps. One, agitation of the desired solvent in the presence of excess of the solid complex. Two, dilution of a definite volume of the saturated solution to the approximate color concentration desired. Three, determination of the extinction at a particular wave length. From this extinction data and the previously prepared calibration curve, the exact concentration of the complex could be calculated. By this method results showed a maximum deviation from the mean of 5 percent, this in the range of 0.001 to 0.00003 moles of the complex.

Transmittancy measurements were made with a General Electric recording spectrophotometer and a Cenco spectrophotometer; the former was used only for the calibration absorption spectra.

IV. THE APPLICATION OF SUBSTITUTED 1,10-PHENANTHROLINE COMPLEXES IN THE QUANTITATIVE ESTIMATION OF VARIOUS ANIONS.

Since Blau discovered that certain of the ferroin complexes were insoluble[2], very little use has been made of the fact. The semi-quantitative data obtained by Taylor[5] on the solubilities of several of the complexes suggest some valuable applications of these complexes as precipitatants in the quantitative separations of various anions. In the present study anions separable

by use of nitro-ferroin were investigated. In view of the fact that very small amounts of the anions unite with the complex cations to form voluminous precipitates, centrifugal methods were applied. The method was applied to ions difficultly separated in the usual methods of their analysis, namely perchlorate and chlorate, persulfate and sulfate, periodate and iodate, and ferrous and ferric iron.

Precipitation and separations were carried out in conical shaped, standard Goetz centrifuge tubes containing a calibrated portion for receiving the precipitate. The centrifuge was a laboratory model known as Type SB equipped with a rheostat for controlling the speed of rotation. The proper conditions of speed of rotation, time of rotation, concentrations of reagents, and range of application were established for each of the anions studied.

Working in the range of 0.5 mg. of the anion salts, excellent reproductibility was attained, the average deviation on series of synthetic samples being within 2 percent. This accuracy was obtained in the presence of large amounts of added ions.

Bibliography

1 Blau, F., Ber., **21**, 1077 (1888).

2 Blau, F., Monatsh., **19**, 647 (1898).

3 Burstall, F. H., J. Chem. Soc., 1662 (1938).

4 Willink, H. D. T., and Wibaut, J. B., Rec. trav. chim. **54**, 275 (1935).

5 Taylor, W. H., Thesis, Doctor of Philosophy, University of Illinois (1941).

Vita

The author was born on October 4, 1919, at Fenton, Illinois. He attended the public schools of that vicinity and was graduated from the high school in Erie, Illinois. In September, 1937 he entered Hope College which granted him the Bachelor of Arts degree in June, 1941. In September, 1941 he enrolled in the graduate school of the University of Illinois. He held a teaching assistantship in the Analytical Division of the Department of Chemistry at the University of Illinois from September, 1941 until June, 1942 and was then appointed to the Aeration Processes Fellowship in Chemistry, which fellowship he has held until the present time. For the summer of 1943 he was employed at the Illinois State Geological Survey, Urbana, Illinois, as a research assistant in the Geochemical section.

The author is a member of the American Chemical Society, Alpha Chi Sigma, and Sigma Xi.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0331